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Transient absorption spectroscopy on spiropyran monolayers using nanosecond pump–probe Brewster angle reflectometry

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Self-assembled monolayers of 11-(3',3'-dimethyl-6,8-dinitrospiro[chromene-2,2'-indoline]-1'-yl) undecanoic acid (amphiphilic spiropyran) at the air–water interface are studied using Brewster angle reflectometry. Transient kinetics of the spiropyran to merocyanine conversion are recorded in a UV-pump, VIS-probe configuration. By varying the probe wavelength using an optical parametric oscillator, we are able to reconstruct absorption spectra of intermediate states with a time-resolution of 10 nanoseconds, limited by the temporal convolution of the two laser pulses. After UV irradiation, spiropyran converts to merocyanine in two stages. The first occurs within a timescale of several tens of nanoseconds and is heavily convoluted with the system response time, whereas the second stage occurs over a few hundred nanoseconds. During the rise time there is a small red shift in the transient absorption spectrum of ~20 nm. We assign the red shift and the slower kinetics to the isomerization of a merocyanine isomer *cis* about the central methine bond to those that are *trans* about the same bond.

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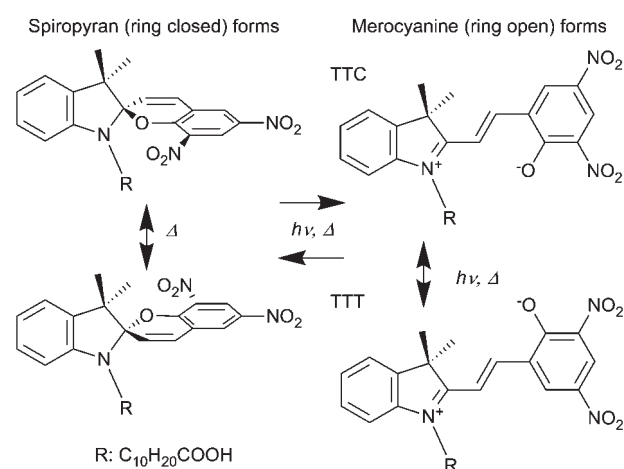
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Introduction

Spiropyran (SP) to merocyanine (MC) conversion (Scheme 1)^{1–3} in thin films and monolayers has attracted a lot of attention in recent years because of potential applications in photoswitching devices. Studies include light-induced phase transitions that induce conformational and pressure changes,^{4–6} and changing the wettability of surfaces.^{7,8} Other works use SP photoswitching to alter surface properties for electrodes on gold to bind proteins,⁹ in biopolymer films¹⁰ and hybrid surface architectures.¹¹

Despite this wide range of research, studies on the fundamental photochemical properties are scarce. This is mainly because thin films and monolayers are hard to monitor in transmittance because they are so thin that they cause only

very small phase shifts in light passing through them and have inherently low absorbance due to their short pathlength. Several techniques that overcome these difficulties have been successfully applied. On metallic surfaces, surface plasmon resonance (SPR)^{12–14} and polarization modulation Fourier transform infrared spectroscopy (PM-FTIR) can be applied.¹⁵ Waveguides¹⁶ and cavity ring-down spectroscopy (CRDS) setups increase the optical pathlength of the sample by allowing the light to travel through the monolayers multiple



Scheme 1

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times.^{17,18} Ellipsometry has been used to study thin SP films.^{19,20}

Brewster angle microscopy (BAM), a special case of ellipsometry, was independently developed by Meunier *et al.* and Möbius *et al.* as a tool to study monolayers.^{21–23} Therefore, it is ideally suited for monitoring SP dynamics in monolayers. BAM is based on the fact that p-polarised light is fully refracted if it is incident on a surface at Brewster's angle. If a monolayer is present at the interface of the surface then a small amount of light is reflected with an intensity dictated by the refractive index of the monolayer. Changes in the complex refractive index alter Brewster's criteria, leading to changes in the amount of light reflected. Capturing this reflected beam on a CCD camera gives high contrast images of the probed interface on an inherently dark background. Previously we have shown that BAM is a useful tool for studying photodynamics in SP thin films and monolayers.^{24,25}

Brewster angle reflectometry (BAR), that is reflectometry in the vicinity of Brewster's angle, was used to study transient kinetics of SP monolayers on functionalised fused silica²⁶ and self-assembled monolayers at the air–water interface.²⁷ One drawback of the methods applied was the lack of spectral resolution in the kinetic studies due to the limitation of available probe wavelengths from the probe lasers used. Our current work expands on these techniques by measuring transient absorption kinetics at different probe wavelengths, generated by an optical parametric oscillator (OPO) pumped by a neodymium yttrium aluminium garnet (Nd-YAG) laser, in order to reconstruct spectra of transient states with nanosecond time resolution.

Experimental

Brewster angle reflectometer

Two types of BAR systems are used in this work. The primary BAR apparatus used for transient kinetic measurements has been described previously.²⁷ The second BAR is a modified NanoFilm EP³ BAM that was used to verify monolayer conditions and measure Brewster's angle as a starting point for simulations.^{26,28} Both systems and recent modifications are described below.

The most notable change to the primary setup is that an OPO (Spectra-Physics MOPO-SL pumped by a Quanta-Ray Pro 270-10 pulsed Nd-YAG laser) is used as a probe light source. This allows tuning the probe light wavelength from 440 nm to 705 nm and 715 nm to 1850 nm. The pulse width of this light is 4–7 ns depending on the wavelength. The probe beam is attenuated by various neutral density filters to keep it constant over the OPO tuning range. Fig. 1 shows the setup of this BAR apparatus. Briefly, a cylindrical lens focuses the probe beam (p-polarized by a high extinction, 1×10^{-8} , Glan–Taylor polarizer) into a strip on the bulk liquid surface. That way the beam has varying angles of incidence making the reflected beam diverge over this range of angles. As the approximate centre of the laser beam is incident at Brewster's angle, reflectivity will

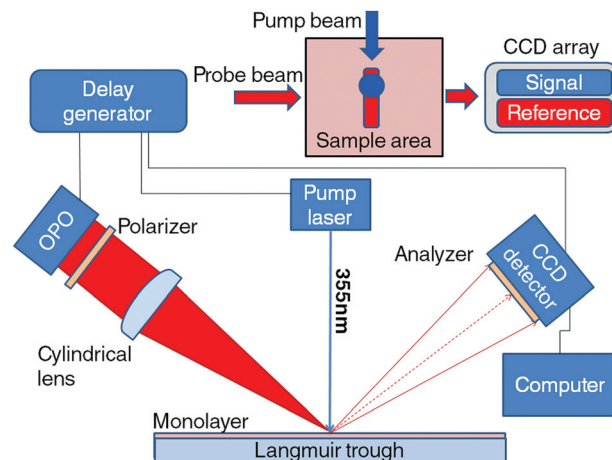


Fig. 1 Setup of the pump-probe Brewster angle reflectometer. The top right insert shows the applied method of self-referencing.

be minimized there. According to Fresnel's equations for p-polarized light, this results in a parabolic reflectivity increase around Brewster's angle.²⁶

The reflected light is collected with a CCD camera (DU420-BV, Andor Technology, cooled to $-85\text{ }^{\circ}\text{C}$ for dark current suppression). The imaging area is a two dimensional array of pixels. This allows the separation of the readout to two vertical strips for self-referenced measurements. One half measures the intensity profile of probe light that is reflected from a UV-pumped (354.7 nm, 8 ns pulse, 2nd harmonic from a Litron NANO-S-60-30 Nd-YAG laser) region of the sample. The other half monitors light from a non-irradiated part. In this way we can directly measure the shifting of Brewster's angle in a one shot self-referenced experiment. This prevents shot to shot noise due to beam profile changes or noise from vibrations in the laboratory from influencing the measurements.

The pump laser is equipped with a variable attenuator that can be used to vary the output energy between 0–10 mJ. A plano-convex lens is used to focus the pump laser to a spot size of $\sim 2\text{ mm}$ diameter on the monolayer.

Transient kinetics are measured by varying the pump-probe delay time using two delay generators (Stanford Research Systems DG535 and Berkley Nucleonics Corporation BNC-465). The nanosecond time-resolution is limited by the temporal convolution of pump and probe laser pulses.

A photodiode (Thorlabs DET 200, 50 Ω terminated, read out by a Tektronix TDS 2014B oscilloscope) is used to measure the relative output power of the pump and probe beams. In that way, we can account for shot to shot fluctuations in pump energy to improve the signal to noise ratio. Additionally it is used to verify the timing of pump and probe signals so as to correct delay time jitter.

The second system is essentially a NanoFilm EP³ BAM that is equipped with nanosecond laser excitation (354.77 nm, 5 ns pulse, 2nd harmonic from a Lotis LS-2134UTF Nd-YAG laser). It is possible to make kinetic measurements with this system, however in the current work it is simply used to image the

state (homogeneity) of the monolayer under identical conditions used for kinetic studies with the primary setup. The built-in EP³ goniometer, which has a 0.01° angle resolution and a reproducibility of 0.001°, makes it possible to establish the Brewster angle of the monolayer very accurately. The precision of this value is important to get better estimations of monolayer thickness and initial refractive index from simulations.^{26,27}

Sample preparation

A linear, Teflon Langmuir trough and a Hamilton micro-syringe are cleaned using chloroform, ethanol, methanol, and deionised water. The spreading solution is prepared using ACS Spectro-photometric grade chloroform (stabilized with 0.5–1.0% ethanol) supplied by Sigma Aldrich without further purification. As the bulk liquid sub-phase we use deionised water (ELAGA Lab Water, Purelab option-Q). The chloroform-spiropyran spreading solution is deposited drop by drop with the needle parallel and as close as possible to the surface without actually touching it.

Amphiphilic spiropyran, 11-(3',3'-dimethyl-6,8-dinitrospiro [chromene-2,2'-indoline]-1'-yl) undecanoic acid, was synthesized from 2,3,4-trimethylindolenium 11-bromoundecanoic acid and 3,5-dinitrosalicylaldehyde *via* a two-step substitution and a condensation reaction as previously described.^{26,28}

Results and discussion

Theoretical considerations

Data analysis and simulations are done analogously to previous work.²⁷ Briefly, the reflectivity and absorption changes of the monolayer can be derived from Fresnel's equations.^{24,26,28} The relation between angular shifts and absorption is linear for initially transparent monolayers. Our simulations and calculations have shown that it is possible to independently determine the changes of the real and imaginary part of the complex refractive index

$$\tilde{n} = n + i\kappa \quad (1)$$

of the monolayer from the behaviour of Brewster's angle minima. Angular shifts are linear in respect to changes of κ , while changes in measured intensity at Brewster's angle are mainly caused by changes in n .

Absorbances are then calculated from κ values using Beer-Lambert's law²⁹

$$Abs = \frac{4\pi}{\lambda} \kappa d \quad (2)$$

where d is the thickness of the monolayer and λ is the probe wavelength. As absorbances are usually supplied in decadic logarithmic base this value will be divided by 2.303.

Monolayer kinetics and time resolved spectra

Fig. 2 shows the kinetics of absorbance changes of a monolayer with a surface area of 0.29 nm² per spiropyran molecule.

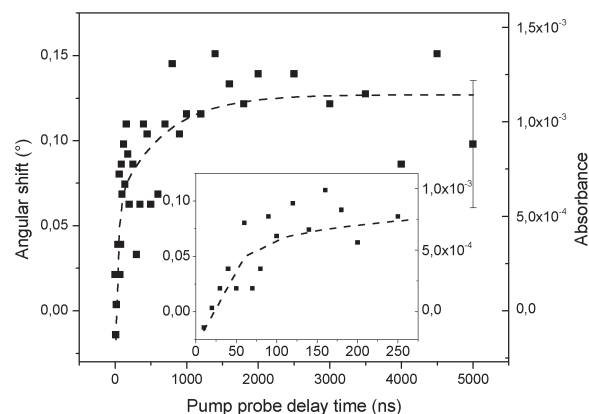


Fig. 2 Kinetic trace of the absorbance change in a spiropyran monolayer probed at 555 nm with its biexponential fit. The error bar of the last data point indicates the maximal expected statistical error, estimated from pre t_0 measurements under same conditions. Axis legends of the insert are identical to the main graph.

For this measurement the OPO was set to 555 nm, the maximum of the merocyanine absorbance peak in chloroform solution (Fig. 3). From biexponential fitting

$$A = A_0 - A_1 e^{-\frac{t}{\tau_1}} - A_2 e^{-\frac{t}{\tau_2}} \quad (3)$$

we find a fast, $\tau_1 = 33 \pm 11$ ns, and a slow, $\tau_2 = 650 \pm 217$ ns, component in the conversion kinetics. The amplitude of the fast component A_1 is twice as big as that of the slow component A_2 . The fact that the total absorbance is lower than the previous results for kinetics at 532 nm suggests that the merocyanine peak is blue shifted in a monolayer on water compared to chloroform solution. This solvatochromism can be attributed to the higher polarity of water.^{1,30} This blue shift is confirmed in the current work (*vide infra*).

Combining kinetic traces collected with different probe wavelengths allows us to reconstruct transient spectra at different pump-probe delay times. Fig. 4 shows the monolayer spectrum at 1 μ s pump-probe delay time obtained with this

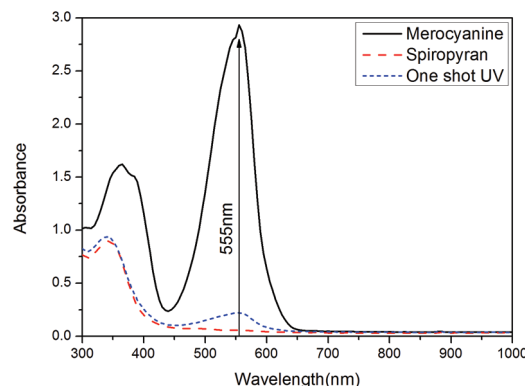


Fig. 3 UV-Vis spectra of dark adapted merocyanine, completely photobleached spiropyran and the merocyanine state after irradiation with one 10 mJ pump pulse at 355 nm. Measurements are made in a 0.5 cm pathlength quartz cuvette.

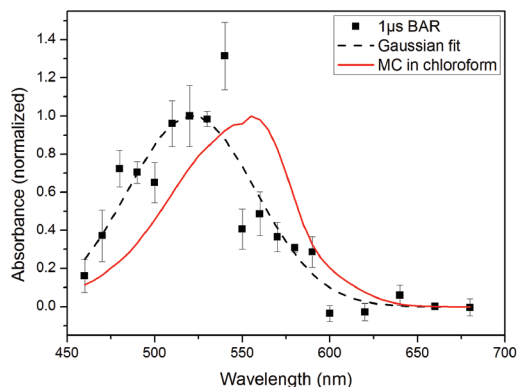


Fig. 4 Comparison of normalized UV-Vis and BAR spectra. The BAR spectrum is measured at a delay time of 1 μ s. Each data point shown is the average of five measurements with its standard error.

method compared to a spectrum obtained in chloroform. The absorption maximum is estimated by fitting a single Gaussian peak to the spectrally resolved data. Comparing these two spectra we find a solvatochromatic blue shift of about 35 nm, which is consistent with the merocyanine being in a more polar environment.¹

Fig. 5 shows the transient absorption spectra at different pump-probe delay times. Following the growth of the merocyanine peak from the system response time (20 ns) to the plateau region (1 μ s), we observe a gradual red shift with prolonged pump-probe delay times. This red shift amounts to \sim 20 nm from the 100 ns pump-probe delay time to the saturated conversion. It is not possible to fit peaks to the data from pump-probe delay times below 100 ns. This is because the expected peak is supposedly smaller than the statistical error of our measurements.

From these results, we can conclude that the conversion of spiropyran to the final merocyanine composition occurs in two stages. Previously, it was proposed that the slower component may be the result of the isomerization of the ring-open merocyanine *cis* about the central methine bond to merocyanine

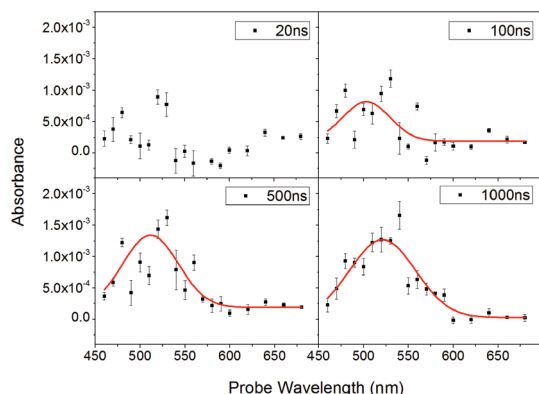


Fig. 5 Transient absorption spectra at different pump-probe delay times between the lower limit of 20 ns and the plateau region after 1 μ s. Each data point is the mean of five measurements with its standard error. Lines are Gaussian fits that indicate the expected peak area.

isomers that are *trans* about this bond.²⁷ However, from NMR data we also know that there are two isomers (TTC and TTT) for this particular molecule in chloroform solution, with more than 70% TTC in equilibrium.^{1,2} This ratio of TTC to TTT is in good agreement with the two amplitudes of the double exponential fit discussed in Fig. 2. Therefore the second component of the kinetics could, in principle, be due to *cis-trans* conversions between TTC and TTT. However, the interconversion between these two forms occurs on a timescale of 10 ms at 243 K,² so it should be too slow to account for the current observations.

The latter rise is associated with a spectral shift of 20 nm, which is a little less than is observed for similar *cis-trans* conversions in stilbene (\sim 30 nm)³¹ and the π - π^* transition of azobenzene (\sim 40 nm).³² For chromene derived mero-forms it has been observed that a mixture of isomers *trans* about the terminal methine bond, but *trans* and *cis* about the terminal methine bond, has a red shift of \sim 7 nm compared to the pure *trans* component.³³ Similar shifts have been observed for *cis-trans* isomerizations in terminal methine bonds of spiropyran derived merocyanines.³⁴

In the current case, in view of the observed spectral shifts and with knowledge of the isomerization rate between the TTC and TTT isomers of \sim 10 ms,² we consider that the \sim 20 nm shift currently observed is most likely due to isomerization from an isomer *cis* about the central methine to one *trans* about that bond. In any event, we can state with some confidence, based upon our spectroscopically resolved data, that the longer component of the kinetic traces seen presently and previously²⁷ is associated with the red shift. Furthermore, this red-shift is consistent with merocyanine isomerization reactions that are slower in the monolayer, taking 100 s of nanoseconds compared to a solution where similar transformations take a few picoseconds.³⁵ We propose that this retardation is due to constricted motion and geometry in the densely packed monolayer.

Fig. 6 shows absorbance and angular shifts for different pump laser fluences. Measurements are taken using 555 nm probe light. By normalising the angular shifts to a pump

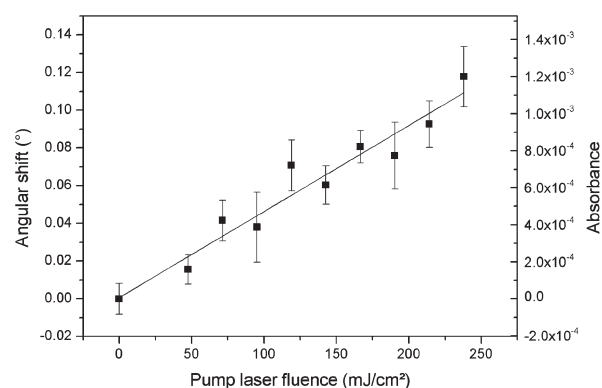


Fig. 6 Angular shift and corresponding absorbance at 1 μ s pump-probe delay time for 555 nm probe light for different pump laser fluences. Statistics are mean and standard error of five measurements at each data point.

power output, we could significantly decrease deviations from the linear fit compared to previous results.²⁷ It is worth commenting on the rather high fluences that the monolayer seems to withstand without apparent damage or saturation of the photochemical conversion process. From the measured transient absorbance, surface coverage and theoretical merocyanine absorbance,¹ we estimate a conversion rate of ~9% at 250 mJ cm⁻². This is consistent with conversions achievable in chloroform solution. Generally, we can state that the quantum yield for coloration of this particular type of spiropyran is very low^{28,36,37} and this explains the high fluences required to achieve this conversion. This is opposite, yet analogous, to the case of spirooxazine ring closure where Bohne *et al.* used laser fluences up to 600 mJ per pulse to photobleach merocyanine isomers due to the very low quantum yield of this process.³⁸

Conclusions

By using the variable wavelength output of an OPO system, we have taken the step from measuring transient angle-resolved reflectivity changes at single wavelengths to collecting absorption spectra over the whole visible region. This method allows the spectroscopic assessment of transient states in monolayers at the air–water interface. Nanosecond time resolution is only limited by the temporal convolution of the OPO and pump laser pulses.

Monolayers of amphiphilic spiropyran convert to merocyanine after UV irradiation. Qualitative measurements have shown that the merocyanine peak red-shifts gradually by ~20 nm during its rise time. We attribute this shift to isomerization of an intermediate that is *cis* about the central methine bond to the final merocyanine isomers that are *trans* about this bond. The isomerization is slower than that observed in solution due to constricted geometry in the densely packed monolayer.

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